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AND USE FOR THE PRODUCTION OF HOLLOW ELEMENTS,
LIKE BOTTLES**

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Molding Compositions Based on Thermoplastic Polyesters

The present invention relates to improved compositions made from thermoplastic polyesters for molding at low temperature.

In particular the invention relates to new polyester compositions having excellent moldability when used at low molding temperatures, less than 90°C, and which yield, at the same time, molded articles having excellent surface characteristics and very good physical properties.

Thermoplastic polyesters, especially polyethylene terephthalate (PET), are used for numerous industrial applications because of their excellent heat resistance, their good resistance to chemical products and their good mechanical and electrical properties. Moreover, their large tonnage production for the textile or film industry leads to a highly competitive sales price.

These substantial advantages unfortunately cannot be fully exploited to the extent that it is impossible to correctly employ these polymers under ordinary molding conditions, i.e., using a low mold temperature below 90°C.

Thermoplastic polyesters, especially PET, have a low crystallization capacity so that, rapidly cooled, especially when injected into a mold kept at a temperature below 90°C, they do not crystallize or only partially crystallize. The articles obtained under these conditions can easily be deformed on mold release. These articles are more susceptible of evolving as a result of crystallization during heating.

The use of compositions based on thermoplastic polyesters for molding under ordinary conditions is therefore based on the need to substantially modify their crystallization kinetics. On leaving the cold mold, the composition must have acquired a crystalline morphology throughout the part.

Numerous companies have sought to modify thermoplastic polyesters and especially PET for the dual purpose of reducing the mold temperatures and increasing molding rates. In particular, the recent studies of the DuPont company can be cited, which are the object of French Patent Application No. 79/04 843, published under No. 2 418 254. This prior art describes a PET reinforced with glass fibers, which was modified by addition to the molding composition of two types of compounds:

- an agent for the formation of crystal nuclei (or nucleating agent), which is a substance chosen from a sodium or potassium salt of a carboxylic acid and a sodium or potassium salt of an organic polymer containing carboxyl groups,

- and an agent for modifying chain mobility (or plasticizer), which is a substance of not very high molecular weight chosen among esters derived from mono- or polycarboxylic aromatic acids and polyols, monoketones, sulfones, sulfoxides, nitriles and amides.

Pursuing research in this area of the art, the applicant found that there are other pairs of products consisting of a nucleating agent and a plasticizer that permit an increase in the crystallization rate of thermoplastic polyesters to a level such that it is possible to use them in a cold mold at temperatures below 90°C with a short dwell time.

More specifically, the present invention relates to improved compositions for molding at low temperature, which contain:

- (a) a thermoplastic polyester,
- (b) a nucleating agent,
- (c) a plasticizer,
- (d) and optionally a filler or reinforcement,

said compositions being characterized by the fact that:

- the nucleating agent (b) is a substance chosen from metal salts derived from organo-phosphonic, organophosphinic and organophosphonous acids,
- the plasticizer (c) is a substance chosen from β -diketones containing 14 to 43 carbon atoms, epoxidized vegetable oils, epoxidized ester derivatives of oleic acid or tall oil fatty acids, esters of the acid known under the commercial name EMPOL.

Thermoplastic polyesters are understood to mean polyesters that soften when exposed to sufficient heat and revert to their original state when cooled to ambient temperature.

In particular, saturated thermoplastic polyesters are preferred and they include saturated aliphatic/aromatic polyesters and fully aromatic polyesters. The expression saturated polyester is understood to include all polyesters that do not contain an olefinic unsaturation in the polymer chain. Saturated thermoplastic polyesters can contain halogen atoms, for example, bromine or chlorine. The use of halogenated polyesters is particularly interesting when one wishes to obtain products having reduced flammability.

The saturated thermoplastic polyesters useful in the present invention can be obtained with the help of a number of methods that are well known to those skilled in the art. These saturated thermoplastic polyesters can be prepared from diols and dicarboxylic acids or from dialkyl esters of dicarboxylic acids in which the alkyl groups can contain 1 to 7 carbon atoms.

Typical diols include aromatic diols or diphenols, for example bisphenol A, phenolphthalein, resorcinol, hydroquinone, catechol, naphthalenediols, stilbene-bisphenol and their mixtures, and saturated aliphatic diols having 2 to 5 carbon atoms, like ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, 1,4-butanediol, 1,5-pentanediol and their mixtures.

It is also possible to use halogenated diols and diphenols. Such halogenated diols and diphenols, for example, include tetrabromobisphenol A, tetrachlorobisphenol A.

Typical carboxylic acids include orthophthalic acid, isophthalic acid, terephthalic acid, naphthalene-1,4- or -2,6-dicarboxylic acids, adipic acid, sebacic acid and their mixtures.

Typical polyesters that are useful in this context include homo- and copolyesters derived from aromatic dicarboxylic acids and saturated aliphatic diols, like polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, polypentylene terephthalate and polyesters containing, in addition to the aforementioned alkylene terephthalate groups, other groups derived from diols and/or diacids.

It should be noted that the typical polyesters useful in this context also include copolyesters derived from aromatic dicarboxylic acids and mixtures of a diol with a triol, like trimethylolpropane and glycerol.

Polyesters that are particularly preferred in this context include PET and its copolyesters containing at least 80 mol% of ethylene terephthalate units. Acids are used as preferred comonomers for the formation of said copolyesters, like isophthalic acid, naphthalene-1,4- or -2,6-dicarboxylic acids, adipic acid, sebacic acid, diols, like propylene glycol, butylene glycol, diethylene glycol, and triols, like trimethylolpropane and glycerol. Naturally the PET and its copolyesters can optionally be used in a mixture.

The employed polyesters generally have an intrinsic viscosity greater than 0.4 dL/g and preferably between 0.5 and 0.8 dL/g. The intrinsic viscosity is measured at 25°C on a polyester solution in orthochlorophenol.

As regards the nucleating agent (b), one generally resorts to alkali, alkaline earth, manganese or zinc salts derived from phosphonic acids of the formula $R_1-P(O)(OH)_2$, phosphinic acids of the formula $R_1R_2-P(O)(OH)$ or phosphonous acids of the formula $R_1-P(O)HOH$, formulas in which R_1 and R_2 , which can be identical to or different from R_1 , each represent a linear or branched alkyl radical having 1 to 6 carbon atoms, an alkenyl radical with 2 to 6 carbon atoms and 1 to 2 olefinic double bonds, a phenyl radical optionally substituted with 1 to 3 alkyl radicals having 1 to 3 carbon atoms, a phenylalkyl radical containing 1 to 3 carbon atoms in the alkyl group and whose benzene ring can optionally be substituted with 1 to 3 alkyl radicals.

Among the acids that correspond to the aforementioned formulas, one can mention in particular the following acids:

- as regards phosphonic acids: methylphosphonic acid, n-propylphosphonic acid, n-amylphosphonic acid, n-hexylphosphonic acid, vinylphosphonic acid, allylphosphonic acid, 1-methylvinylphosphonic acid, 1,3-butadienylphosphonic acid, phenylphosphonic acid, 4-methylphenylphosphonic acid, 2,4-dimethylphenylphosphonic acid, benzylphosphonic acid, 4-methylbenzylphosphonic acid;

- as regards phosphinic acids: dimethylphosphinic acid, di-n-propylphosphinic acid, diphenylphosphinic acid, di(4-methylphenyl)phosphinic acid, methylphenylphosphinic acid, ethylphenylphosphinic acid, dibenzylphosphinic acid;

- as regards phosphonous acids: methylphosphonous acid, ethylphosphonous acid, phenylphosphonous acid, benzylphosphonous acid.

The nucleating agents (c) that are preferably used are sodium, potassium, magnesium, manganese or zinc salts derived from the aforementioned acids.

Among the preferred salts, the following are particularly suitable: calcium phenylphosphonate and sodium diphenylphosphinate.

The amounts of nucleating agent (b) are generally between 0.05 and 10 % by weight relative to the polyester and preferably between 0.1 and 5%.

As regards the plasticizer (c), the suitable products are more precisely:

(i) As regards β -diketones:

- either products of the formula: $R_3-CO-CH_2-CO-R_4$

in which

- R_3 represents a linear or branched alkyl radical having 10 to 20 carbon atoms;

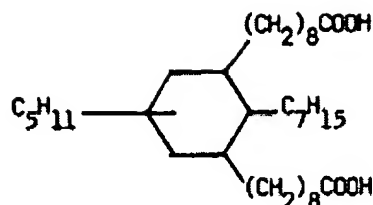
- or products of the formula:

$$\begin{array}{c} \text{R}_3\text{-CO-CH-CO} \\ \quad \backslash / \\ \quad \text{R}_5 \end{array}$$

- R_3 has the meaning already mentioned above;

atoms of the radical so defined being between 3 and 20 atoms; a phenylalkylene radical containing 1 to 14 carbon atoms in the alkyl group and whose benzene ring can optionally be substituted with 1 to 3 alkyl or alkoxy radicals with 1 to 3 carbon atoms; for example 3-stearoyl- γ -butyrolactone, 3-stearoyl- γ -valerolactone, 3-stearoyl- δ -valerolactone, 2-stearoyl-1-tetralone, 2-palmitoyl-1-tetralone;

(iii) As regards esters of the acid EMPOL: alkyl, cycloalkyl or arylalkyl esters, for example methyl, ethyl, benzyl, 4-methylbenzyl esters; EMPOL is an aliphatic diacid containing 36 carbon atoms, whose structure could be the following:



The plasticizers that are suitable include stearylbenzoylmethane, 2-stearyl-1-tetralone, epoxidized soybean oil and benzyl ester of EMPOL.

The amounts of plasticizer (c) are generally between 1.5 and 15 % by weight relative to the polyester and preferably between 2 and 10%.

The fillers or reinforcements (d) that can be added to the compositions of the present invention are highly varied. These can be a fibrous material, like asbestos fibers; carbon fibers; metal or metalloid carbide or nitride fibers, like fibers of silicon carbide, silicon nitride, boron carbide; glass fibers; organic fibers that can resist heat. The filler can also consist of glass microspheres, mica flakes, talc or associations of two or more of the aforementioned materials. Among these fillers, one particularly prefers glass fibers. These glass fibers can be ordinary glass fibers or treated glass fibers, for example, treated with silane and/or chromium. Generally these glass fibers have a diameter between 3 and 30 μm and a length less than 10 mm. The compositions of the invention can contain fillers in an amount that can reach 80% of the weight of the polyester. The amount of fillers is preferably between 20 and 60%.

In addition to the aforementioned constituents, the compositions according to the present invention can contain additives commonly used with polyester resins, like dyes, mold release agents, antioxidants, ultraviolet stabilization agents, and flame retardants.

One can prepare the compositions according to the present invention with the help of any conventional process. For example, they can be prepared by means of introducing constituents (a), (b), (c) and optionally (d) together into an appropriate mixer, extruding the mixed constituents to a continuous strand and cutting the strand into pellets and optionally, if necessary, molding the pellets to the desired shape. One can also prepare these compositions in the manner indicated above as a result of mixing constituent (a) with a masterbatch of constituents (b) and (c) prepared beforehand and optionally filler (d). It should also be noted that the nucleating agent (b) can be used during the preparation of the polyester, either by way of introducing it to the reaction medium or by means of mixing it with the initial reagents (diacid and diol).

The following nonlimiting examples demonstrate how the present invention can be practiced.

Example 1

Polyethylene terephthalate with an intrinsic viscosity equal to 0.680 dL/g is mixed in a kneader under nitrogen at 280°C with calcium phenylphosphonate (2 % by weight relative to polyester) and stearylbenzoylmethane (5 % by weight relative to polyester).

The improvement furnished by the nucleating agent-plasticizer pair can be evaluated by the molding rate or more conveniently with the help of differential thermal analysis as a result of determining, relative to the polyester, only the reduction in crystallization temperature on heating (after having made one or the other polymer amorphous by quenching from the molten state), as well as the increase in crystallization temperature during cooling from a melt.

The results of differential thermal analysis accomplished for heating and cooling rates of 10°C per minute are as follows:

Samples	Crystallization temperature	
	on heating	on cooling
Polyethylene glycol terephthalate alone	149°C	200°C
Polyethylene glycol terephthalate (same as before) + 2% calcium phenylphosphonate + 5% stearylbenzoylmethane	120°C	215°C

Example 2

Mixing of a polyester with an intrinsic viscosity of 0.680 with calcium phenylphosphonate (2 % by weight relative to polyester) and 2-stearyl-1-tetralone (5 % by weight relative to polyester) is accomplished under the same conditions as described for example 1.

Examination with the help of differential thermal analysis, carried out as before, yields the following results:

Samples	Crystallization temperature	
	on heating	on cooling
Polyethylene glycol terephthalate alone	149°C	200°C
Polyethylene glycol terephthalate + 2% calcium phenylphosphonate + 5% 2-stearoyl-1-tetralone	108°C	215°C

Example 3

A composition is prepared in a PRODEX extruder containing a screw 44.45 mm in diameter and 26 D long equipped with a vacuum degassing system ($40 \cdot 10^2$ Pa) at 280°C from 70 parts by weight of polyethylene terephthalate with an intrinsic viscosity of 0.680 with 2 parts by weight (2.86 % by weight relative to polyester) of calcium phenylphosphonate, 5 parts by weight (7.14 % by weight relative to polyester) of epoxidized soybean oil marketed by the company L'AIR LIQUIDE under the name PLASTEON 652 and 30 parts by weight (42.85 % by weight relative to polyester) of glass fibers cut to a length of 6 mm available commercially under the name SILENKA 8082.

The results of differential thermal analysis carried out for heating and cooling rates of 10°C per minute are as follows:

Samples	Crystallization temperature	
	on heating	on cooling
Polyester alone	156°C	200°C
Composition according to the example	116°C	211°C

In order to determine the minimal cooling time before mold release, an annular mold with six ribs is used, regulated at 80°C. This mold is intended to produce a hollow cylinder of limited thickness (1.3 mm), whose interior contains six radial fins of the same thickness. The molding is ejected from the mold by a circular ejector supported on the cylinder (and not supported on the ribs).

The minimum dwell time in the mold for which the part is ejected without deformation and for which the molded product separates from the mold without difficulty is determined.

The following table summarizes the obtained results:

Employed composition	Minimum cooling time before mold release
Polyethylene glycol terephthalate (70 % by weight) Cut glass fiber 6 mm (SILENKA 8082) (30 % by weight)	>20 seconds Impossibility of ejection of the part without deformation
Composition according to the example	1 second

Example 4

Polyethylene terephthalate with an intrinsic viscosity of 0.680 is mixed under nitrogen in a meter at 280°C with calcium phenylphosphonate (2 % by weight relative to polyester) and the benzyl ester of EMPOL 1010 acid (5 % by weight relative to polyester).

Examination with the help of differential thermal analysis, carried out as before, yields the following results:

Samples	Crystallization temperature	
	on heating	on cooling
Polyethylene glycol terephthalate alone	149°C	200°C
Polyethylene glycol terephthalate + 2% calcium phenylphosphonate + 5% benzyl ester of EMPOL acid	132°C	211°C

Claims

1. Improved compositions for low-temperature molding, containing:

- (a) a thermoplastic polyester,
- (b) a nucleating agent,
- (c) a plasticizer,
- (d) and optionally a filler or reinforcement,

said compositions being characterized by the fact that:

- the nucleating agent (b) is a substance chosen among metal salts derived from organo-phosphonic, organophosphinic and organophosphonous acids,
- the plasticizer (c) is a substance chosen among β -diketones containing 14 to 43 carbon atoms, epoxidized vegetable oils, epoxidized esters derived from oleic acid or tall oil fatty acids, esters of the acid known under the commercial name EMPOL.

2. The compositions according to Claim 1, characterized by the fact that the thermoplastic polyester is a polyethylene terephthalate or copolyester containing at least 80 mol% of ethylene terephthalate units.

3. The compositions according to any of the Claims 1 and 2, characterized by the fact that the nucleating agent (b) is chosen among alkali metal, alkaline earth metal, manganese and zinc salts derived from phosphonic acids of the formula $R_1-P(O)(OH)_2$, phosphinic acids of the formula $R_1R_2-P(O)(OH)$ and phosphonous acids of the formula $R_1-P(O)HOH$, formulas in which R_1 and R_2 , which can be identical to or different from R_1 , each represent a linear or branched alkyl radical having 1 to 6 carbon atoms, an alkenyl radical having 2 to 6 carbon atoms and 1 to 2 olefinic double bonds, a phenyl radical optionally substituted with 1 to 3 alkyl radicals having 1 to 3 carbon atoms, a phenylalkyl radical containing 1 to 3 carbon atoms in the alkyl group and whose benzene ring can optionally be substituted with 1 to 3 alkyl radicals.

4. The compositions according to Claim 3, characterized by the fact that the nucleating agent (b) is calcium phenylphosphonate or sodium phenylphosphinate.

5. The compositions according to any of the Claims 1 to 4, characterized by the fact that the plasticizer (c) is chosen from the following products:

(i) β -diketones of the formula:

$R_3\text{-CO-CH}_2\text{-CO-R}_4$ in which:

- R_3 represents a linear or branched alkyl radical with 10 to 20 carbon atoms;
- R_4 represents an alkyl radical of the same type as R_3 with the possibility that R_3 and R_4 are identical or different, a phenyl radical optionally substituted with 1 to 3 alkyl or alkoxy radicals having 1 to 3 carbon atoms, a phenylalkyl radical containing 1 to 6 carbon atoms in the alkyl group and whose benzene ring can optionally be substituted with 1 to 3 alkyl or alkoxy radicals having 1 to 3 carbon atoms;

and $R_3\text{-CO-CH-CO}$ in which



- R_3 has the meaning already given above in Claim 1;
- R_5 represents a divalent radical chosen from: a linear or branched alkylene radical optionally containing one or more chains of the type -O- , -C-O- , -CO- , the total number of



radical atoms so defined being between 3 and 20 atoms; a phenylalkylene radical containing 1 to 14 carbon atoms in the alkyl group and whose benzene ring can optionally be substituted with 1 to 3 alkyl or alkoxy radicals having 1 to 3 carbon atoms;

(ii) epoxidized products having a residual iodine value (g of $I_2/100$ of product) of between about 1 and 13 and a percentage of epoxide oxygen between about 3 and 10, which belong to the group comprising epoxidized linseed oil, epoxidized safflower oil, epoxidized soybean oil, epoxidized wheat germ oil, epoxidized cottonseed oil, epoxidized rapeseed oil, epoxidized peanut oil and epoxidized alkyl esters derived from maleic acid or tall oil fatty acids;

(iii) and alkyl, cycloalkyl or arylalkyl esters of EMPOL acid.

6. The compositions according to Claim 5, characterized by the fact that the plasticizer (c) is chosen from stearylbenzoylmethane, 2-stearyl-1-tetralone, epoxidized soybean oil and a benzyl ester of EMPOL acid.

7. The compositions according to any of the Claims 1 to 6, characterized by the fact that the optional filler (d) is chosen among carbon fibers, metal or metalloid carbide or nitride

fibers, glass fibers, organic fibers that are resistant to heat, glass microspheres, mica flakes, talc and associations of two or more of the aforementioned materials.

8. The compositions according to Claim 7, characterized by the fact that the optional filler (d) consists of glass fibers.

9. The compositions according to any of the Claims 1 to 8, characterized by the fact that they contain

- from 0.05 to 10 % by weight relative to polyester of nucleating agent (b),
- from 1.5 to 15 % by weight relative to polyester of plasticizer (c),
- and optionally from 20 to 60 % by weight relative to polyester of filler (d).